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Corrosion Inhibitors

Geethamani Palanisamy

Abstract

Corrosion is a natural process driven by energy consideration. Inhibition is a preventive measure against corrosive attack on metallic materials. Corrosion inhibitors have been frequently studied, since they offer simple solution for protection of metals against corrosion in aqueous environment. Mineral acids like hydrochloric and sulfuric acids are most widely used in pickling baths to remove the metal oxides formed on the surface. The multidisciplinary aspect of corrosion problems combined with the distributed responsibilities associated with such problems only increase the complexity of the subject. Inhibitors are used in industrial and commercial processes to minimize both the metal loss and acid consumption.

Keywords: corrosion inhibitors, acidic inhibitors, volatile inhibitors, vapor phase inhibitor

1. Introduction

Corrosion is the primary means by which metals deteriorate. Corrosion introduces itself into many parts of our lives [1, 2]. The great majority of us have personal feeling for the importance of corrosion. Far too many have cringed at the emergence of rust holes in the body panels of relatively new automobiles [3]. The outdoor rusting of steel, household and garden appliances is a common fact of life. All have seen the strains on cooking utensils from hot foods or experienced the metallic taste in acid foods stored too long on open cans. That these effects are caused by corrosion is well known [4]. The glaring example related to corrosion is the appearance of cracks in certain portions of Taj Mahal, was due to steel dowels embedded inside had extensively corroded and rusted leading to fractures in the stoned [5]. However, corrosion is just as common in other material classes such as ceramics, plastics and rubber. Since, practically all environments are corrosive to some degree and are major contributing causes of material failure and also are a large economic cost to the society [6].

2. Historical background

Corrosion can be viewed as a universal phenomenon, omnipresent and omnipotent. It is there everywhere, air, water, soil and in every environment, we encounter [7]. Known to people as rust, corrosion is an undesirable phenomenon which destroys the luster and beauty of the materials and lessens their life. Indian government spending around 3.5% Lakscrores of the nation's GDP per annum for losses of corrosion [8]. Recent studies estimate that, not only in India, other countries also rise their funds for demand of corrosion inhibitors [9].

Corrosion costs manifest in the form of premature deterioration or failure necessitating maintenance, repairs and replacement of damaged parts.. Corrosion has a vast environmental and economic impact on all the surfaces of national infrastructure like highways, bridges, buildings, chemical processing units, waste water treatment and virtually on all metallic objects in our day to day life use [10]. Other than material loss, corrosion interferes not only with environment, also affects human safety and industrial operations severely. Awareness to corrosion and adaptation of timely and appropriate control measures hold the key in the abatement of corrosion failures [11].

3. Corrosion definition

The spontaneous oxidation of metal is termed as corrosion [12], that is, Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. The medium in which the metal undergoes corrosion is termed as corrosive or aggressive medium. Corrosion products formed are chemical compounds containing the metal in the oxidized form with the exception of gold and platinum, all other metals corrode and transform themselves into substances similar to the mineral ores from which they are extracted [13].

4. Adverse economic and social effects of corrosion

The corrosion affects severely on the safe, reliable and efficient operation of equipment and structures than the simple loss of a mass of metal [14]. Failures of all kind of machineries and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be listed below:

Nuclear plant shutdown due to failure, for example, nuclear reactor during decontamination process.

- Replacement of corroded equipment resulting in heavy expenditure.
- High cost preventive maintenance such as painting.
- Loss of efficiency.
- Loss of product from a corroded container.
- Safety requirement measures from a fire hazard or explosion or release of toxic product.
- Health problems, for example, drinking water contamination with lead is likely due to corrosion.

5. Chemistry of corrosion

In general, metals are having unique properties like opaque, lustrous, conductivity, malleable and ductile in nature and are readily forms metallic bonds with other metals and ionic bonds with non-metals [15, 16]. The metals that have overlapping conduction bands and valence bands in their electronic structure.

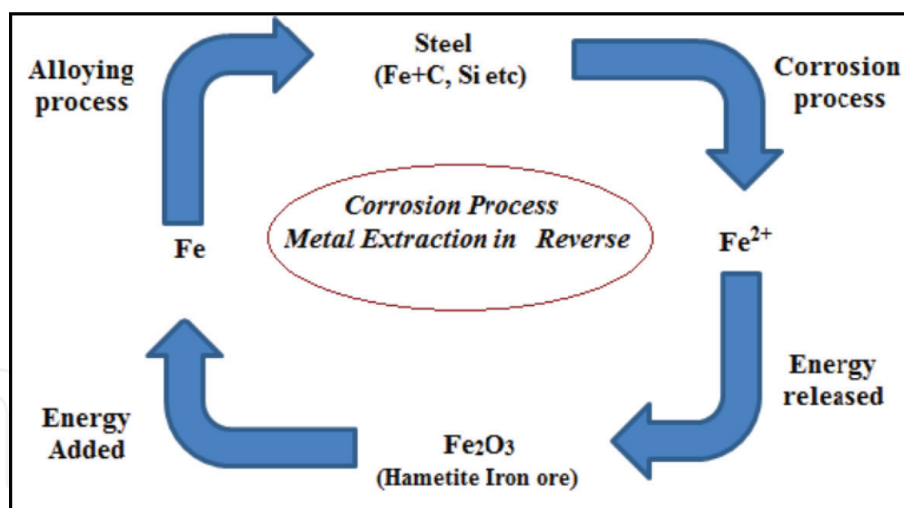


Figure 1.
 Corrosion cycle process.

Metals are obtained from their ore by the expenditure of large amounts of energy. Metals store heat as potential energy during the smelting and refining process and release this energy during the corrosion process after reacting with the environment. These metals can therefore be regarded as being in a metastable state and will tend to lose their energy by reverting to compounds more or less similar to their original states, for example the starting material for iron and steel making and the corrosion product rust has the same chemical composition (Fe_2O_3).

The energy stored during melting and released during corrosion supplies the driving potential for the corrosion process to take place. Since most metallic compounds, and especially corrosion products, have little mechanical strength, a severely corroded piece of metal is quite useless for its original purpose [17]. Metals such as Mg, Al, Zn, and Fe which require larger amount of energy for refining are more susceptible to corrosion than metals which require lesser amount for refining such as gold, silver, platinum. A corrosion cycle is shown below (**Figure 1**).

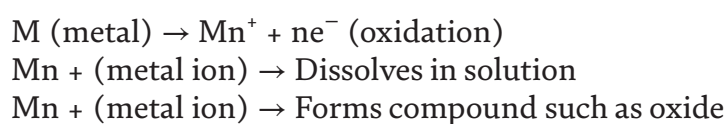
6. Classification

Corrosion has been classified into different methods. They are

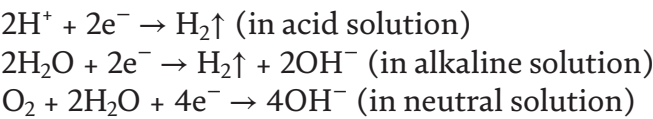
- Low temperature corrosion and high temperature corrosion (or)
- Electrochemical corrosion and chemical corrosion (or)
- Wet and Dry corrosion.

Wet corrosion occurs when the metal is in contact with an electrolytic conducting liquid or when two dissimilar metals or alloys are either immersed or dipped partially in the electrolytic conducting solutions. This is always associated with low temperature conditions. The corrosion process involves two reactions.

At anode:



At Cathode:



Dry corrosion takes place mainly through the direct chemical action of atmospheric gases and vapors present in the environment 30. This is most often associated with high temperature.

7. Forms of corrosion

Corrosion can manifest itself in many forms such as uniform corrosion or general corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, selective leaching, erosion corrosion, stress corrosion, corrosion fatigue and fretting corrosion [18]. In order to improve the understanding between corrosion and design engineers it is classified into two broad categories. They are expressed in flow chart (Figure 2).

7.1 General corrosion

This general corrosion also called as a uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface or over a large area [19]. The metal becomes thinner and eventually fails.

7.2 Galvanic corrosion

It occurs when a potential difference exists between two dissimilar metals immersed in a corrosive solution. This potential difference produces a flow of electrons between the metals. Several investigations have shown that, galvanic corrosion is directly proportional to the area of the cathodic to the anodic metal [20]. A schematic diagram for galvanic corrosion is shown below(Figure 3).

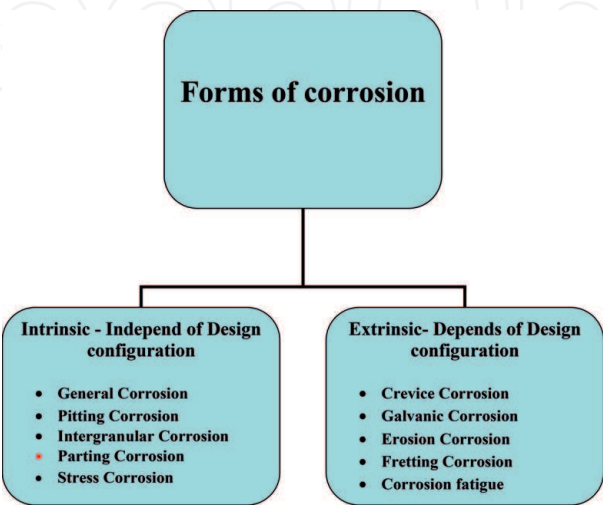


Figure 2. Forms of corrosion.

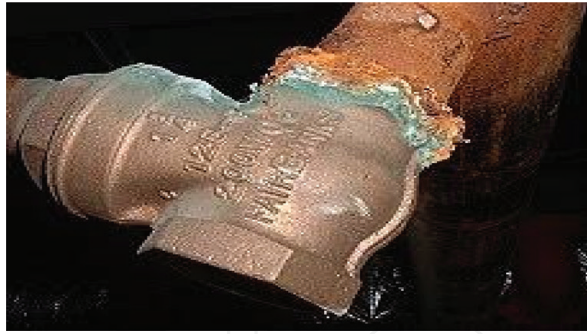


Figure 3.
Schematic representation of galvanic corrosion.

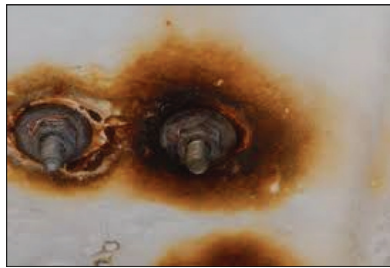


Figure 4.
Schematic representation of crevice corrosion.

7.3 Crevice corrosion or deposit corrosion

This kind of corrosion is attacked generally within crevices associated with small volumes of stagnant solution trapped in holes, surfaces, joints and crevices under bolt and rivet heads (**Figure 4**) [21]. It is also known as deposit or gasket corrosion.

7.4 Pitting corrosion or localized corrosion

Pitting corrosion is a localized attack resulting in the formation of holes in the metals. These holes are relatively small and they look like a rough surface (**Figure 5**), they were sometimes isolated or so close together. Pitting is one of the most destructive and insidious forms of corrosion [22].

7.5 Intergranular corrosion

Most of the metals and alloys are susceptible to intergranular corrosion, when exposed to specific corrosion environment which is shown in the **Figure 6**. Grain boundaries are usually more reactive than grain matrix. Hence localized attack occurs at and adjacent to grain boundaries with relatively little corrosion of the matrix. This type of attack is usually rapid and penetrates deep into the metal resulting in loss of strength and causes catastrophic failures. It is caused by,

- Impurities at the grain boundaries
- Enrichment of one of the elements in the alloy
- Depletion of one of the elements in the boundary area.

7.6 Selective leaching

Selective leaching is the removal of an element from an alloy by corrosion. Selective removal of zinc from brass is a prime example of this form of attack. A similar attack has been observed with other alloys in which iron, aluminum, cobalt and chromium are removed. This type corrosion is undesirable as it yields a porous metal with poor mechanical properties (Figure 7).

7.7 Erosion corrosion

It is the increase of attack of a metal because of relative movement between a corrosive medium and the metal surface. This type of erosion corrosion is usually associated with systems where high velocities of corrosive fluids or gases are encountered.

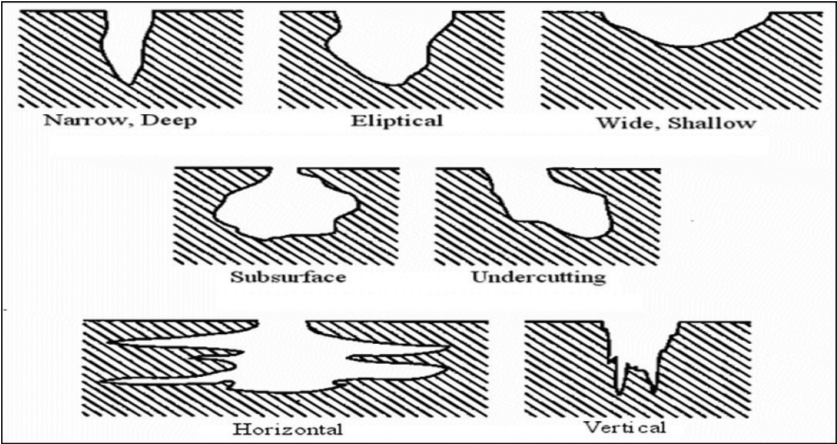


Figure 5.
Schematic representation of pitting corrosion.



Figure 6.
Schematic representation of intergranular corrosion.



Figure 7.
Schematic representation of selective leaching corrosion.

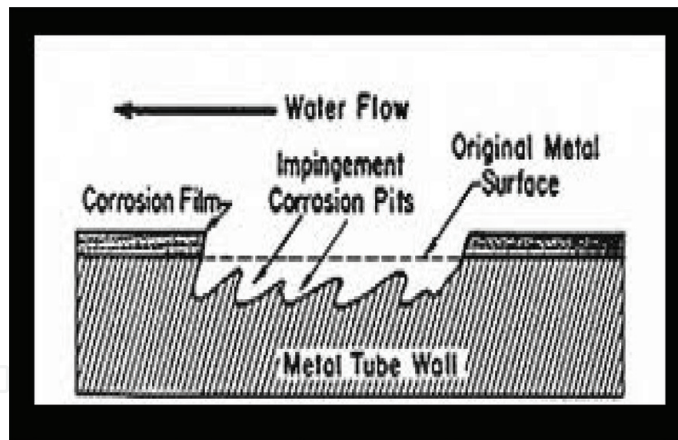


Figure 8.
 Schematic representation of erosion corrosion.

This corrosion can be observed in piping system such as bends, elbows, pumps and condensers, etc. A Schematic representation of erosion corrosion is shown in **Figure 8**. Factors affecting erosion corrosion are nature of surface film, corrosion environment and presence of air bubbles with its size, chemical composition, suspended solids, corrosion resistance and metallurgical properties of metals and alloys.

7.8 Stress corrosion

The cracking of metal or alloy by the combined action of a tensile stress and a corrodent (**Figure 9**) is known as stress corrosion cracking. The susceptibility to stress corrosion cracking is due to certain metallurgical factors such as,

- Chemical composition
- Preferential orientation of grains
- Composition and distribution of precipitates
- Dislocation structure and environmental factors and structure of metal.

7.9 Corrosion fatigue

It is defined as, “the reduction of the fatigue strength due to the presence of corrosive environment”. Corrosion fatigue occurs due to the combined action of tensile and compressive stress alternatively. Fatigue occurs at lower stress in corrosive environment.

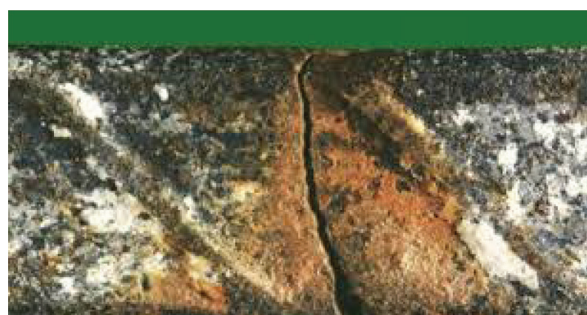


Figure 9.
 Schematic representation of stress corrosion.

7.10 Fretting corrosion

Fretting is a wear phenomenon enhanced by corrosion. It involves wear of a metal or alloy when in contact with another solid material in dry or humid air. Fretting is the result of abrasive wear surface oxide films, which form a contacting surfaces under load in atmospheric air which is shown in **Figure 10**. The factors which affect fretting corrosion are:

- Magnitude of relative motion
- Temperature
- Environment
- Metallurgical factors

Due to slight motion such as vibration, surface oxide and underlying metal, gets spoiled. The metal particles as a result of wear get oxidized to hard oxides which act as an additional abrasive medium. Further, the motion grinds the oxides particles thus causing wear.



Figure 10.
Schematic representation of fretting corrosion.



Figure 11.
Schematic representation of cavitation corrosion.

7.11 Cavitations corrosion

It is a special type of erosion corrosion which is caused due to the formation of vapor bubbles in a corrosive environment near a metal surface and when the

bubbles collapse, attack arises for example, hydraulic turbulence, ship propellers, etc. It is similar to pitting corrosion but the surface is rough and has many close spaced pits (**Figure 11**).

8. Factors influencing corrosion

The extent and rate of corrosion depend on nature of the metals and the environments.

8.1 Nature of the metal

1. Position of metals in EMF series
2. Overvoltage
3. Relative area of anodic and cathodic parts of the metal
4. Purity of the metal
5. Physical nature of the metal
6. Nature of the surface film
7. Solubility of products
8. Volatile corrosion products.

8.2 Nature of the environment

- Temperature range
- Humidity of air
- Impurities in water
- Presence of suspended particles in atmosphere
- Influence of pH
- Nature of dissolved gases, dissolved salts, pollutants, etc.
- Conductance of the corroding medium
- Formation of oxygen concentration cell
- Flow velocity of process steam
- Polarization of electrodes.

9. Factors controlling corrosion rate

Certain factors tend to accelerate the action of a corrosion cell which includes the establishment of well-defined locations on the metal surface for the anodic

and cathodic reactions. Metals having a more positive (noble) potential in the galvanic series will tend to extract electrons from a metal which is in a more negative (base) position in the series and hence accelerate its corrosion when in contact with it [23]. Aggressive ions such as chloride tend to prevent the formation of protective oxide films on the metal surface and thus increase corrosion.

9.1 Corrosion rate

The rate of corrosion is expressed based on the loss per unit time. The rate at which the attack takes place is of prime importance and is usually expressed in one of the two ways:

- Weight loss per unit area per unit time, usually mdd (milligrams per square decimeter per day).
- Decrease in thickness per unit time, that is, rate of penetration or the thickness of metal lost. This may be expressed in American units, mpy (mils per year) or in metric units or mmpy (millimeters per year).

10. Corrosion control methods

Corrosion is destructive and silent operating processes. It poses problems to big as well as small industries. Since corrosion is inevitable to eliminate but can be minimized by adopting certain anticorrosion method rather than preventing it [24]. The practical methods available for the protection of metal against corrosion are diverse. They may be broadly based on,

- Modification of metal
- Modification of design
- Modification of corrosive environment
- Modification of metal environment potential
- Use of inhibitors
- Modification of surface

These methods can be used individually or in combination.. One of the best known methods of corrosion protection is using corrosion inhibitors instead of using the various methods to avoid or prevent destruction or degradation of metal surface. Because using inhibitors is following stand up due to low cost and practice method [25, 26].

11. Inhibitors

An inhibitor is a chemical substance or combination of substances which when added in very low concentrations in a corrosive environment effectively prevents or

reduces corrosion without significant reaction with the components of the environment. Concentrations of corrosion inhibitors can vary from 1 to 15,000 ppm (0.0001 to 1.5 wt %). Inhibitors play a vital role in closed environmental systems that have good circulation so that an adequate and controlled concentration of inhibitor is ensured [27]. Such conditions can be met, for instance in cooling water recirculation systems, oil production, oil refining, and acid pickling of steel components. One of the more recognizable applications for inhibitors is in antifreeze for automobile radiators. Inhibitors may be organic or inorganic compounds and they are usually dissolved in aqueous environments [28].

11.1 Definition of inhibitor

An inhibitor is a substance which when added to an environment in small concentration minimizes the loss of metal, reduces the extent of hydrogen embrittlement, protects the metal against pitting, reduces over pickling and acid fumes resulting from excessive reaction between the acid and basic metals and reduces acid consumption. They reduce corrosion by either acting as a barrier by forming an adsorbed layer or retarding the cathodic, the anodic or both processes [10]. A schematic representation of inhibitor process is shown in **Figure 12**.

Any corrosion retardation process or the reduction in the oxidation rate of the metal by addition of a chemical compound to the system is caused by corrosion inhibitors. Inhibitors are often easy to apply and offer the advantage of in-situ application without causing any significant disruption to the process. The use of corrosion inhibitors is one of the best methods of combating corrosion [11].

In order that they can be used effectively, three factors must be considered, namely:

- Identification of the corrosion problems.

Generally, the components of a corrosion cell (anode, cathode, electrolyte and electronic conductor) may be affected by corrosion inhibitors in order to reduce corrosion. The inhibitor may cause:

- Anodic inhibition (increasing the polarization of the anode)
- Cathodic inhibition (increasing the polarization of the cathode)
- Resistance inhibition (increasing the electrical resistance of the circuit while forming a thin or thick deposit on the surface of the metal)
- Diffusion restriction (restricting the diffusion of depolarizers, e.g., DO).

However there are several factors to be considered when choosing an inhibitor.

- Cost of the inhibitor.
- Toxicity of the inhibitor can cause ill effects on human beings and other living species.
- Availability of the inhibitor determines the selection of it.
- Inhibitor should be environment friendly.

In order to avoid or reduce the corrosion of metallic materials, inhibitors used in cooling system must satisfy the following criteria

- It must give good corrosion protection at a very low concentration of inhibitor.
- It must protect all exposed materials from the attack of corrosion.
- It must remain efficient in extreme operating conditions (higher temperature and velocity).
- In case of an under or over dosage of inhibitor, corrosion rate should not increase drastically.
- The inhibitor or reaction products of the inhibitor should not form any deposits on the metal surface particularly at locations where heat transfer takes place.
- It should suppress both uniform and localized corrosion.
- It should have long range effectiveness.
- It should not cause toxicity and pollution problems.

11.2 Definition of inhibition

One of the extensively studied topics in the field of corrosion is inhibition. Inhibition is a process of preventive measure against corrosive attack on metallic materials. Chemical compounds may be used which, when added in small concentrations to an aggressive environment, are able to decrease corrosion of the exposed metal [12].

11.3 Corrosion inhibitors

Corrosion inhibitors can be any forms (solids, liquids and gases). Based on the solubility or dispersibility in fluids corrosion inhibitors are selected which are to be inhibited. Corrosion inhibitors have been found to be effective and flexible means of corrosion mitigation. The use of chemical inhibitors to decrease the rate of corrosion processes is quite variable. Corrosion inhibitors are used in oil and gas exploration and production, petroleum refineries, chemical manufacturing, heavy manufacturing, water treatment and product additive

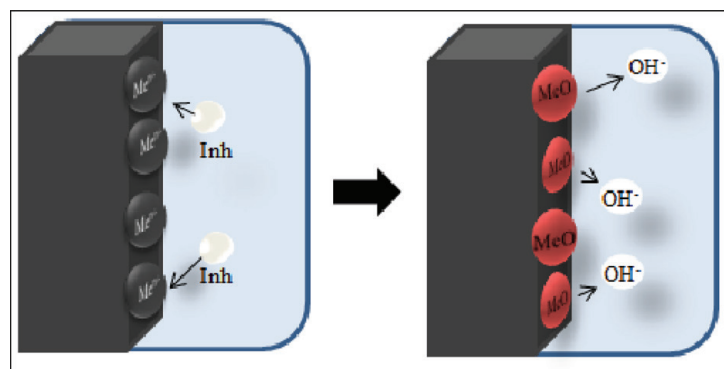


Figure 12.
Schematic representation of inhibition process.

industries [29]. In the oil extraction, processing and chemical industries, corrosion inhibitors have always been considered to be the first line of defense. A great number of scientific studies have been devoted to the subject of corrosion inhibitors [30, 31].

11.4 Role of inhibitors

Organic and inorganic compounds constitute a large class of corrosion inhibitors, which as a general rule; affect the entire surface of a corroding metal when present in sufficient concentration. Most of the organic/inorganic compounds containing elements of groups V B, VI B or functional groups of the type amine, carbonyl and alcoholic groups are more effective corrosion inhibitors. The inhibitor is adsorbed on the entire metal surface of the corroding metal and so prevents attack from the corrosion. Organic inhibitors are adsorbed on the metals surface [32]. The inhibitors may be considered as two fundamental types, they are, those which form a protective barrier film on anodes or cathodes by reaction between the metal and the environment. This type of inhibitors function in neutral or in some cases, alkaline solution in which the main cathodic reaction is an oxygen reduction reaction in which the corroding metal surface is covered by a film oxide or hydroxide.

Another type is initially adsorbed directly onto the metal surface by interaction between surface charges and ionic and/or molecular dipole charges. This division of inhibitor types results principally from the pH of the solution where they operate. Inhibitors must be present in a minimum concentration for them to be fully effective. This is very common with anodic inhibitors.

The efficiency of organic inhibitors can be improved in the presence of certain halogen ions. Halogen ions are also known to inhibit corrosion to some extent in acid solutions. The efficiency of the corrosion inhibition is in the order; $I^- > Br^- > Cl^-$. Fluoride does not show inhibition characteristics. Synergism of halogen ions can be attributed to the fact that the metal adsorbs halogen ions whose charge shifts the surface in a negative direction, thereby increasing adsorption of the cationic organic inhibitor. Being able to discover possible compounds that can be used as corrosion inhibitors requires a lot of hard work, innovation and laboratory analysis/synthesis [33].

Certain halogen ions present in the organic inhibitors are known to inhibit corrosion to some extent in acid solutions. The efficiency of the corrosion inhibition is following in the order of $I^- > Br^- > Cl^-$. Fluoride does not shows any inhibition characteristics. Synergism of halogen ions can be attributed to the fact that the metal adsorbs halogen ions whose charge shifts the surface in a negative direction, thereby increasing adsorption of the cationic organic inhibitor.

11.5 Classification of corrosion inhibitors

Corrosion inhibitors are briefly classified (**Figure 13**) as follows,

11.5.1 Based on electrode process

11.5.1.1 Anodic inhibitors

An anodic inhibitor increases the anodic polarization and hence moves the corrosion potential to the cathodic direction and hence also called as passivating inhibitors. Anodic inhibitors such as chromates, phosphates, tungstates and other ions of transition elements with high oxygen content are those that stifle the

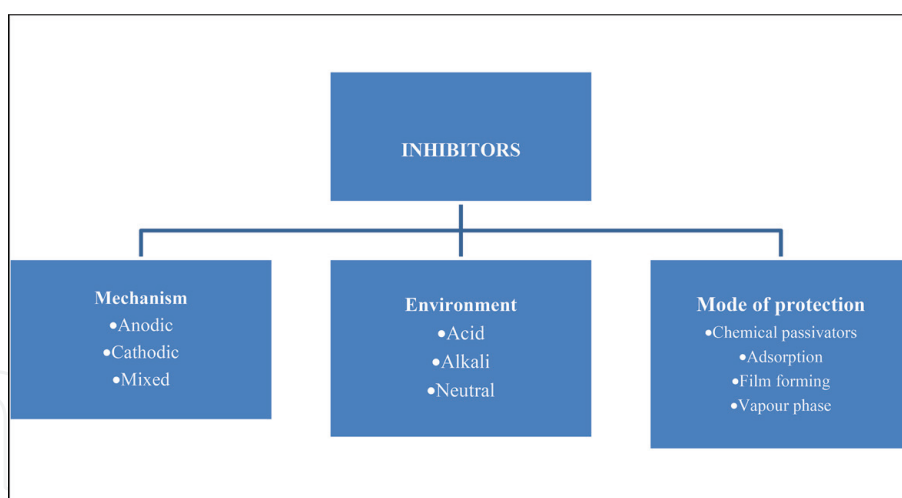


Figure 13.
Classification of corrosion inhibitors.

corrosion reaction occurring at the anode by forming a sparingly soluble compound with a newly produced metal ion. They are adsorbed on the metal surface forming a protective film or barrier, thereby reducing the corrosion rate. Anodic inhibitors build a thin protective film along the anode and increasing their potential and thus slow down the corrosion reaction [34].

Although, this type of control is affected, yet it may be dangerous since severe local attack can occur, if certain areas are left unprotected by depletion of the inhibitors. A number of inorganic inhibitors such as orthophosphates, silicates, etc. fall under anodic type. Even though anodic inhibitors are widely used, a few of them have some undesirable property. If such inhibitors are used in very low concentrations, they cause stimulation of corrosion such as pitting and for this reason anodic inhibitors are denoted as dangerous.

There are two types of passivating inhibitors.

- The oxidizing anions such as chromates, nitrites and nitrates that can passivate steel in the absence of oxygen.
- The non-oxidizing ions such as phosphates, tungstates and molybdates that require the presence of oxygen to passivate steel.

In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason, it is essential to monitor the inhibitor concentration.

11.5.2 Cathodic inhibitors

Cathodic inhibitors reduce corrosion by slowing the reduction reaction rate of the electrochemical corrosion cell. This is done by blocking the cathodic sites by precipitation. Cathodic inhibitors are effective when they slow down the cathodic reaction. Elements As, Bi and Sb are referred to as cathodic poisons which reduce the hydrogen reduction reaction rate and lower the overall corrosion rate. Removal of oxygen from the corrosive environment will significantly decrease the corrosion rate. This can be done through

- The use of oxygen scavengers such as sodium sulfite and hydrazine which react with the oxygen and remove it from the solution

- Vacuum de-aeration or
- Boiling to lower the dissolved oxygen concentrations.

Cathodic inhibitors shift the corrosion potential to the anodic direction. [35, 36] Here the cations migrate towards the cathode surfaces where they are precipitated chemically or electrochemically and thus block these surfaces. The inhibiting action of cathodic inhibitors takes place by three mechanisms,

- **Cathodic poisons:** The cathodic reduction process is suppressed by impeding the hydrogen recombination and mode of protection discharge but increase the tendency of the metal to be susceptible to hydrogen induced cracking.
- **Cathodic precipitates:** Compounds such as calcium, magnesium will precipitate as oxides to form a protective layer which acts as a barrier on the metal surface.
- **Oxygen scavenger:** These compounds react with oxygen present in the system to form a product and reduce corrosion. For example, As^{3+} and Sb^{3+} on dissolution of Fe in acids.

11.5.2.1 Mixed inhibitors

These inhibitors retard both the anodic and cathodic processes involved in the corrosion process and are therefore called mixed inhibitors [37]. They are typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly. Anodic inhibitors are, for the most part, dangerous inhibitors, especially if their concentrations are too less. But cathodic inhibitors are generally safe. Mixed inhibitors are less dangerous than pure anodic inhibitors, and in number of cases they may not increase the corrosion intensity. The most common inhibitors of this category are the silicates and the phosphates. Such inhibitors will have the more advantage that they control both the cathodic and anodic corrosion reactions.

11.5.3 Based on environment

11.5.3.1 Acidic environment inhibitors

11.5.3.2 Inorganic inhibitors

The compounds such as As_2O_3 , Sb_2O_3 have been reported as inhibitors in acid media. In this case, the protection is due to the reduction of electro positive ions and deposition on the metal surface and lowering of the over voltage of main cathodic depolarization reaction [38]. Recently it is shown that the addition of heavy metal ions such as Pb^{2+} , Ti^+ , Mn^{2+} and Cd^{2+} is found to inhibit corrosion of iron in acids.

11.5.3.2.1 Organic inhibitors

Organic compound containing oxygen, nitrogen, sulfur with multiple bonds have been reported as good corrosion inhibitors. Many organic inhibitors such as amines, aldehydes, alkaloids, nitro and nitroso compounds have been studied and tried as corrosion inhibitors [39]. Organic inhibitors can be anodic, cathodic and mixed type based on its reaction at the metal surface and potential. These are effective depending upon its size, carbon chain length, aromaticity, conjugation and nature of bonding atoms [40].

11.5.3.3 Alkaline inhibitors

Metals, which form amphoteric oxides, are prone to corrosion in alkaline solutions. Many organic compounds are often used as inhibitors for metals in basic solutions [41]. Compounds such as thiourea, substituted phenols, naphthol, β -diketone, etc., have been used as effective inhibitors in basic solutions due to the formation of metal complexes.

11.5.3.4 Neutral inhibitors

Inhibitors which are effective in acidic solutions do not function effectively in neutral solutions, since the mechanism is different in the two solutions [42–44]. In neutral solutions, the interaction of inhibitors with oxide covered metal surface and prevention of oxygen reduction reaction at the cathodic sites takes place. Such inhibitors protect the surface layers from aggressiveness. Some surface active chelating inhibitors have been found to be efficient inhibitors in near-neutral solutions [45].

11.5.4 Based on mode of protection

11.5.4.1 Chemical passivators

Substances which usually have a sufficiently high equilibrium potential (redox or electrode potential) and sufficiently low over potential decrease corrosion rate on attainment of passivity and are called chemical passivators [46].

Example, nitrites are used as inhibitors for antifreeze cooling waters. Chromates are mostly used as inhibitors for recirculating cooling waters. Zinc molybdate is used as an inhibiting pigment for paints.

11.5.4.2 Adsorption inhibitors

These represent the most widely used class of inhibitors. In general, they are organic compounds which get adsorbed on the metal surface and provide a blanketing effect over the entire surface, that is, both in cathodic and anodic cases. Generally they effect both cathodic and anodic reactions equally, but in many cases the effect may not be equal. These are commonly used in the acid pickling of hot rolled products in order to remove the black mill scale and are thus known as pickling inhibitors [47–49].

Examples: Compounds containing lone pairs of electrons such as nitrogen atoms in amines, quinolines, sulfur atoms in thio compounds and oxygen atoms in aldehydes.

11.5.4.3 Film forming inhibitors

In contrast to the adsorption inhibitors which form the straight forward adsorbed film of the inhibiting species, many substances called film forming inhibitors, appear to stop corrosion by forming a blocking or a barrier film of a material other than the actual inhibiting species itself. Such materials tend to be specific either to the cathode or to the anode. Zinc and calcium salts are the most common examples of cathodic film forming inhibitors. Benzoate is the common example of anodic film forming inhibitors, which inhibit corrosion during voyages [50].

11.5.4.4 Vapor phase inhibitors

Atmospheric corrosion of metals in closed spaces as in parcels during storage and shipment can be prevented by the use of certain substances called vapor phase inhibitors also called as volatile inhibitors [51–56]. These are substances of low but significant vapor pressure. The vapor comes in contact with the surface of the metal and the adsorption of the inhibitor takes place. The moisture then hydrolyses it and releases protective ions which have corrosion inhibiting properties. **Figure 14** shows the schematic representation vapor phase inhibitors.

Examples,

Dicyclohexylamine chromate and benzotriazole for protecting copper.

Phenyl thiourea and cyclohexylamine chromate for brass.

Dicyclohexylamine nitrite for ferrous and nonferrous part.

11.5.4.5 Volatile inhibitors or vapor phase inhibitors

Volatile corrosion inhibitors (VCIs) are compounds which transferred in a closed environment to the site of corrosion by volatilization from a source (**Figure 15**). If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion leading to excessive corrosion. Example, Molybdenum oxide (MoO_3), the oxidation corrosion product of molybdenum is volatile. In closed vapor process (shipping containers), volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene amine are used as volatile corrosion inhibitors [52].

11.5.4.6 Synergistic inhibitors

These are single inhibitor which is used in cooling water systems. More often, a combination of inhibitors (anodic and cathodic) is used to obtain better corrosion protection properties [56]. Examples include chromate-phosphates, polyphosphate-silicate, zinc-tannins, and zinc-phosphates.

11.5.4.7 Precipitation inhibitors

These are compounds that forms precipitates on the metal surface, thereby providing a protective film. The most common inhibitors of this category are the silicates and the phosphates. For example, Sodium silicate, is used in many domestic water softeners to prevent the occurrence of rust [57, 58].

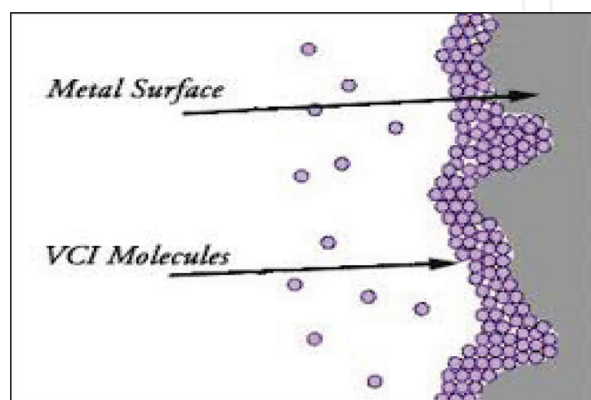


Figure 14.
Schematic representation of vapor phase inhibitors.

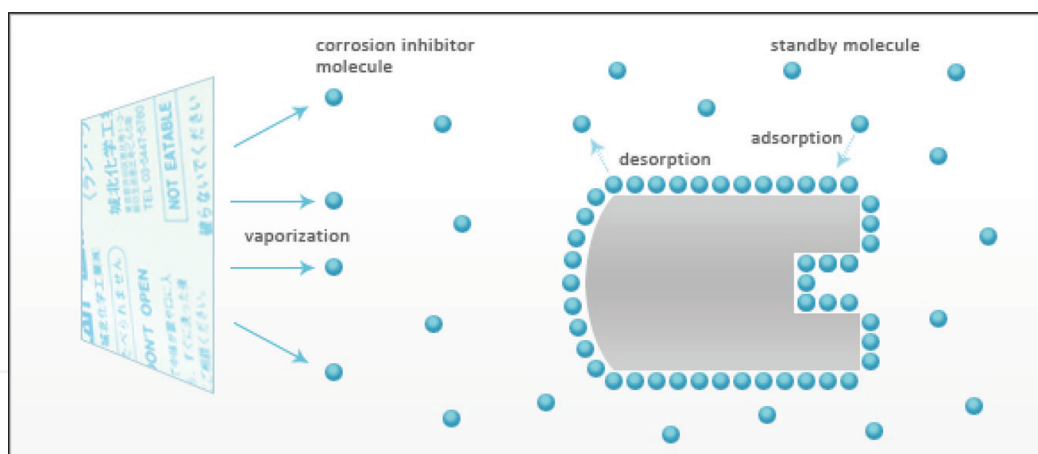


Figure 15.
Schematic representation of volatile inhibitors.

11.5.4.8 Green corrosion inhibitors

There is no clear and accepted definition of “environmentally friendly” or “green” corrosion inhibitors. In practice, corrosion inhibition studies have become oriented towards human health and safety considerations. For this purpose recently, the researchers have been focused on the use of eco-friendly compounds such as plant extracts, expired nontoxic medicines, etc. which contains many organic compounds [59–61]. Amino acids, alkaloids, pigments and tannins are used as green alternatives for the toxic and hazardous compounds. Due to biodegradability, eco-friendliness, low cost and easy availability and the extracts of some common plants and medicinal plant and its products have been studied as corrosion inhibitors for various metals and alloys under different environmental conditions.

11.6 Mechanism of corrosion inhibition

The mechanism of the inhibition process of the corrosion inhibitors under consideration is mainly due to the adsorption. The phenomenon of adsorption is influenced by the nature and surface charge of the metal and by chemical structure of inhibitors. The surface charge of the metal is due to the electrical field which emerges at the interface on immersion in the electrolyte [62–64].

Inhibition usually results from one or more of the following mechanisms

- Adsorption of corrosion inhibitors onto metals

The inhibitive performance is usually depends on the fraction of the surface covered, θ with adsorbed inhibitor. But, at low surface coverage ($\theta < 0.1$), the effectiveness of adsorbed inhibitor species in retarding the corrosion reactions may be greater than at high surface coverage.

- Presence of surface charge on the metal

Adsorption of inhibitor on the metal surface may be due to dipoles of the adsorbed species or electrostatic force of attraction between ionic charges and the electric charge on the metal at the metal/solution interface.

- Effect of functional group and structure

Usually, when the metal contains vacant electron orbitals of low energy such as transition metals. Inhibitors can also bond to metal surfaces by electron transfer to the metal to form a coordinate type of bond. Electron transfer from the adsorbed

species is favored by the presence of relatively loosely bound electrons. Example: Anions and neutral organic molecules containing lone pair of electrons or electron systems associated with multiple bonds especially triple bonds or aromatic rings. The electron density at the functional group is directly proportional to the inhibitive efficiency in a series of related compounds.

- Inhibitor and water molecules interaction

Adsorbed water molecule are removed from the metal surface due to displacement reaction of adsorbed inhibitor molecules and increases the size of hydrocarbon part of inhibitor, which leads to decreasing solubility and increasing adsorption ability. This is consistent with the increasing inhibitive efficiency observed at constant concentrations with increasing molecular size in a series of related compounds.

- Interaction between adsorbed inhibitor species

Lateral interactions between adsorbed inhibitor species may become significantly increases the surface coverage and the adsorbed species. These interactions either attractive or repulsive. If attractive interactions occur between molecules containing large hydrocarbon components (e.g., n-alkyl chains), may the chain length increases. Then the increasing Van der Waals attractive force between the adjacent molecules leads to stronger adsorption at high coverage.

- Adsorbed inhibitors reaction

The adsorbed corrosion inhibitor may react usually by chemical or electrochemical reduction to form a product that may exhibit inhibitive action. A process of added small quantity of substance is called as primary inhibition and that due to the reaction product is secondary inhibition. In these cases, the inhibitive efficiency may increase or decrease with time, it depends on the extent of secondary inhibition is more effective than the primary inhibition. For example, sulfoxides can be reduced to sulfides which are more efficient inhibitors.

- Diffusion barrier formation

The adsorbed inhibitor molecules may form a surface layer that acts as a physical barrier to the diffusion of ions or molecules and to or from the metal surface, and hence retard the rate of corrosion reactions. A surface film of these types of inhibitors affects both anodic and cathodic reactions.

- Blocking of reaction sites

The blocking decreases the number of metal atoms at which corrosion reactions can occur. During this, mechanisms of the reactions are not affected, and the Tafel slopes of the polarization curves remain unaffected [65].

- Electrode reactions

Corrosion reactions involve the formation of adsorbed intermediate molecules with surface metal atoms. The adsorbed inhibitors will forbid the formation of these adsorbed intermediates, but the electrode processes may proceed by alternative paths through intermediates containing the inhibitor. In this process, the inhibitor act as catalyst and remain unchanged. Such reactions of inhibitor are characterized by an increase in the Tafel slope of the anodic dissolution of the metal. Inhibitors may also retard the rate of hydrogen evolution on the metals by affecting the mechanism of the reaction [66]. This effect has been observed on iron in the presence of inhibitors such as phenylthiourea, aniline derivatives, benzaldehyde derivatives and pyridinium salts [67].

- Electrical double layer alteration

The adsorption of ions or species that can form ions on metal surfaces will change the electrical double layer at the metal/solution interface, and this will affect the rates of the electrochemical reactions [68]. The adsorption of cations such as quaternary ammonium ions and protonated amines makes the potential more positive in the plane of the closest approach to the metal ions from the solution. This positive potential shift hinders the discharge of the positively charged hydrogen ions. These effects have been observed with sulfosalicylate ions and the benzoate ions [69, 70].

Conclusion

- Corrosion is a natural process which reduces the binding energy in metals and degrades the useful properties of materials.
- The end result of corrosion involves a metal atom being oxidized, whereby it loses one or more electrons.
- The corrosion manifests itself as a break-up of bulk metal to metal powder. Corrosion.
- Corrosion inhibitors are a great effective method of preventing corrosion.
- The knowledge of the method of the action, facilitates the choice of the inhibitors, improves efficiency, avoids the process is impaired and side effects.
- It is important in the choice of inhibitor whatever may be the method, ascertain the subsequent effects of this towards the environment.
- The environmental friendly inhibitors have shown excellent results, outperforming conventional inhibitors.

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